



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b>  <b>A23B 7/148, 7/152</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/11913</b>  <b>(43) International Publication Date:</b> 22 August 1991 (22.08.91)
<b>(21) International Application Number:</b> PCT/AU91/00049 <b>(22) International Filing Date:</b> 13 February 1991 (13.02.91) <b>(30) Priority data:</b> PJ 8619 13 February 1990 (13.02.90) AU <b>(71) Applicants (for all designated States except US):</b> THE BROKEN HILL PROPRIETARY COMPANY LIMITED [AU/AU]; 140 William Street, Melbourne, VIC 3000 (AU). <b>(71) Applicant (for all designated States except US):</b> DARA-TECH PTY. LTD. [AU/AU]; 6th Floor, 409 St Kilda Road, Melbourne, VIC 3004 (AU). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> DALGLEISH, Paul, Joseph [AU/AU]; 2 Greville Court, Forest Hill, VIC 3131 (AU). RIGBY, Geoffrey, Raymond [AU/AU]; 36 Creswell Avenue, Charlestown, NSW 2290 (AU). JONES, Brett, Arthur [AU/AU]; 26 Fourth Street, Seahampton, NSW 2286 (AU). LITTLE, Colin, Ross [AU/AU]; 2 Brayside Avenue, Sherbrooke, VIC 3789 (AU).		<b>(74) Agent:</b> SMITH SHELSTON BEADLE; 207 Riversdale Road, Hawthorn, VIC 3122 (AU). <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CONTROLLED ATMOSPHERE GENERATION IN HORTICULTURAL APPLICATIONS  <b>(57) Abstract</b>  <p>A method and apparatus is described for monitoring and controlling the concentrations of oxygen and carbon dioxide in the atmosphere of a storage container or cool storeroom. The invention uses a knowledge of (a) the oxygen usage and carbon dioxide production rates of the produce stored and (b) the void volume and air leakage rate of the container or cool storeroom to determine a purge gas flowrate and oxygen concentration which will maintain the preset concentrations of oxygen and carbon dioxide. A permeable membrane gas separation unit is preferably used to provide the purge gas which is generated by compressing air on one side of the membrane permeable to oxygen to produce an oxygen deficient retentate and an oxygen rich permeate.</p>		

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**TITLE: CONTROLLED ATMOSPHERE GENERATION  
IN HORTICULTURAL APPLICATIONS**

This invention relates to use of controlled gas atmospheres in storage containers and cool stores and in particular to the controlled atmosphere storage and transport of horticultural produce.

With increasing production and over-supply of many varieties of fruit and vegetables at peak periods, significant effort is being devoted to establishing the conditions required for effective controlled atmosphere storage of a wide range of fresh horticultural products. In addition to land based storage, emphasis is also being placed on extending the storage life of produce for containerised export. Seasonality can therefore be overcome as produce can be drawn from "in season" areas to provide out-of-season demand in "off season" areas. Also countries which do not have a large horticultural capacity can be supplied with fresh produce without having to rely on the expense and availability of air freight.

Since fresh horticultural produce requires oxygen for respiration, a reduction in the availability of oxygen (compared to that in air) in storage after harvest will slow down the rate of respiration and therefore extend storage and transport life. Similarly high carbon dioxide levels will maintain produce quality for longer periods by combating bacterial and fungal growth.

Ethylene is a natural ripening hormone produced by the fruit. Its production and hormonal effect can be reduced by low oxygen concentrations and by controlling the carbon dioxide to a level suited to the produce.

Controlled atmosphere facilities have used various techniques for establishing the initial gas composition in a cool store or container, including pure nitrogen (either liquid or cylinder storage) or an external gas generator. Liquid nitrogen systems offer the advantage of rapid reduction in  $O_2$  concentration by the use of high gas flows but require cryogenic storage facilities and assurance of

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supply. This mode of operation can also be expensive for small growers where the stores are opened at regular intervals.

Open flame and catalytic combustion generators utilising hydrocarbons as fuel provide gases low in  $O_2$  concentration. However, these gases contain  $CO_2$ , water vapour and other impurities, including ethylene which need to be removed either before the gas is passed to the cool store or by circulation of gases from the cool store.

Pressure swing adsorption (PSA) systems utilising molecular sieve adsorbants to separate nitrogen from air are capable of producing nitrogen with low oxygen contents (<1%). However, the PSA systems, as with the nitrogen production from exhaust gases, are mechanically complex and do not provide a sufficiently flexible adjustment of flowrates and  $N_2$  concentrations.

In addition, PSA systems are generally unacceptable for use with containers due to their size and weight.

Membrane separation systems can produce nitrogen enriched air (up to 99.5%  $N_2$ ) from compressed air based on the preferential permeation of oxygen through a non-porous polymeric membrane. Membrane systems are simple to operate and provide a level of flexibility in adjustment of flowrates and gas compositions not readily available in other gas generators.

Maintenance and control of the atmosphere during storage and transport require the use of recirculation or purging systems. Combustion type generators generally utilise recirculation of the store gases through an external scrubber utilising lime, activated charcoal or molecular sieve adsorbent to remove and control  $CO_2$  produced by respiration.

Existing systems for land based cool stores for products such as apples and pears rely on a constant purge gas flowrate for the establishment of the required  $O_2$  levels. After establishment of the desired  $O_2$  level, it is generally maintained by admission of air as desired. It

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has been found that for containers, more specialised control is necessary, especially for more valuable fruits and vegetables and that both purge gas  $O_2$  compositions and flowrates need to be varied during the maintenance period to maintain the desired control of  $O_2$  and  $CO_2$  concentrations. These flowrates and compositions depend on container parameters such as leakage, temperature, produce properties and external atmospheric conditions.

It has been found that parameters such as leakage rates in containers vary with purge gas flowrates and external atmospheric conditions, especially pressure variations. Therefore any control system must be capable of allowing for any large variations in climatic pressure and temperature conditions if it is to be capable of transport from cooler climates in the southern hemisphere to the northern hemisphere and return.

None of the presently available systems control or allow for varying leakage and respiration rates or control  $CO_2$  and  $O_2$  levels in an interactive way.

Thus it is an object of the present invention to provide a method of monitoring and maintaining the atmosphere in a container or store room (once the initial conditions have been established) which accounts for variations in leakage and produce respiration and controls the  $CO_2$  and  $O_2$  level by responding to any changes in gas composition.

Thus in accordance with the invention, there is provided a method for monitoring and controlling the atmosphere of a container or cool store, said atmosphere being established at predetermined oxygen and carbon dioxide set points, comprising the steps of :

- (a) using predetermined data on,
  - (i) the void volume and air leakage rate of the container, and
  - (ii) the oxygen usage and carbon dioxide production of the produce in the container, to determine a purge gas flowrate and oxygen

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concentration which will maintain the oxygen and carbon dioxide concentration set points and supplying purge gas accordingly,

- (b) after a predetermined time, monitoring actual carbon dioxide levels in the container or store room and determining new values of the purge gas flowrate and oxygen concentration which will achieve the oxygen and carbon dioxide concentration set points and supplying purge gas at the determined flowrate and oxygen concentration, and
- (c) repeating step (b) for duration of the time at which the atmosphere is to be maintained at said predetermined concentration set points.

In another aspect, the invention provides an apparatus for monitoring and controlling the atmosphere of a container or cool store once predetermined oxygen and carbon dioxide concentration set points have been established comprising:

- (a) means to determine from
  - (i) the void volume and air leakage rate of the container and
  - (ii) oxygen usage and carbon dioxide production of the produce in the container, a purge gas flowrate and oxygen concentration which will achieve the predetermined oxygen and carbon dioxide concentration set points,
- (b) means to supply purge gas at the flowrate and oxygen concentration determined in (a),
- (c) means to monitor the oxygen and carbon dioxide concentration in the container after a predetermined time and determining new values for the purge gas flowrate and oxygen concentration to achieve the predetermined set points, and
- (d) means to adjust the purge gas flowrate and oxygen concentration to the values determined in (c).

The present invention also resides in the produce

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conditioned in a controlled atmosphere maintained by the method or apparatus of the invention as defined above.

Provided the leakage rate is below a critical level, any fluctuations in the leakage rate can be detected by variations of  $O_2$  and  $CO_2$  levels from the predicted levels. Similarly if respiration rates are higher or lower than expected and the  $CO_2$  level is above or below its predicted level, then the purge gas flowrate concentration can be adjusted to produce the desired  $CO_2$  level.

Preferably the purge gas is generated by compressing air on one side of a membrane permeable to oxygen to produce an oxygen deficient retentate and an oxygen rich permeate. The oxygen concentration of the purge gas can be varied for any given flowrate by changing the pressure drop across the membrane. Similarly the flowrate can be varied for any given oxygen concentration by changing the inlet pressure to the membrane. Hence there is independent control of flowrate and  $O_2$  concentration in the purge gas.

Separate purge gas systems may be used to establish the initial atmosphere and for maintenance of the atmosphere. This allows the gas generation and control system for the maintenance of the atmosphere to be small enough so that the complete unit is easily fitted and removed from the container.

If a membrane system is used to establish the initial atmosphere in the container it is preferable to use a variable purge gas rate and oxygen concentration. During this initial "pull-down" step the pressure drop across the membrane and the flowrate of purge gas are adjusted such that the oxygen concentration of the purge gas is about one half the instantaneous oxygen concentration in the container. By having a variable flowrate and oxygen concentration in the purge gas it has been found that the desired atmosphere is established quicker than if a constant flowrate and oxygen concentration is used.

Excessive ethylene levels can cause deterioration of some produce and it is often desirable to maintain the

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concentration at levels of less than 1 ppm to prolong storage life. Although continuously supplying purge gas in accordance with the invention reduces the build-up of these gases, an ethylene and volatile esters scrubber may be used in the container to achieve the desired levels.

A pressure equalisation measure such as a breather bag may be used inside the container (preferably above the produce) to minimise air leakage caused by localised temperature or pressure changes.

The foregoing and other features, objects and advantages of the present invention will become more apparent from the following description of the preferred embodiment and accompanying drawings of which:

Figure 1 is a flow chart of the computer program for control of a controlled atmosphere container;

Figure 2 is a schematic layout of a refrigerated container and membrane maintenance control unit;

Figure 3 is a schematic layout of a membrane gas generation system.

Figure 4 illustrates the difference in "pull down" time between constant purge gas flowrate and a variable purge gas flowrate in accordance with the invention;

Figure 5 is an example of  $O_2$  and  $CO_2$  container concentrations using the method of the invention;

Figure 6 is a typical relation between purge gas flowrate and container leakage; and

Figure 7 shows a typical retentate flow vs oxygen concentration for a membrane cartridge.

Figure 8 is a process flow diagram of a typical container or cool store.

The control system incorporates a knowledge of the produce respiration and container parameters to control the container gas compositions preferably utilising a membrane gas generation system. The system optimises gas flow and composition by employing a mass balance which is described below with reference to Figure 8.

The following assumptions are made with respect to the



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## mass balance

- (1) Perfect mixing, gas leaving the container has the same composition as the bulk gas in the container.
- (2) No carbon dioxide enters the container through leakage or the membrane purge.
- (3) Oxygen is consumed by respiration, at the same rate that carbon dioxide is produced.

Concentration balance for oxygen:

$$\frac{VdC_{O_2}}{dt} = P.C_p + L.20.9 - (P + PCO_2 + L).C_{O_2} - R$$

Concentration balance for carbon dioxide:

$$\frac{VdC_{CO_2}}{dt} = PCO_2.100 + R - (P + PCO_2 + L).C_{CO_2}$$

Integrating and solving these equations, yields the final equations used in the computer control of refrigerated shipping containers and cool stores.

$$O_2^t = \frac{(P.C_p + L.20.9 - R)(I - E) + O_2^{\circ}.E}{(P + PCO_2 + L)}$$

$$CO_2^t = \frac{(PCO_2.100 + R)(I - E) + CO_2^{\circ}.E}{(P + PCO_2 + L)}$$

$$\text{where } E = \exp - \frac{(P + PCO_2 + L)t}{V}$$

## NOMENCLATURE

$O_2^t, CO_2^t$ :	Oxygen and carbon dioxide concentrations in the container or store after time t (%).
$O_2^{\circ}, CO_2^{\circ}$ :	Initial oxygen and carbon dioxide concentrations (%).
P :	Membrane purge flowrate (L/m).
$PCO_2$ :	Supplementary carbon dioxide flow (L/m) (if required).
$C_p$ :	Oxygen concentration in membrane purge flow (%).
$C_{O_2}$ :	instantaneous $O_2$ concentration, %.
$C_{CO_2}$ :	instantaneous $CO_2$ concentration, %.

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L	:	Leakage of gas into the container or store (L/m).
R	:	Produce respiration (L/m).
V	:	Container or store void volume (L).
t	:	Time (minutes).
R'	:	Specific respiration (ml/kg.h), normally quoted.
W	:	Weight of produce (kg).

All of these variables, excepting  $O_2^t$  and  $CO_2^t$ , are input to the control program.

Produce respiration is determined experimentally for a particular produce, and is quoted in ml/kg.h ( $R'$ ). The respiration used in these equations is obtained as follows:

$$R = \frac{R' \cdot W \cdot 100}{60000} \quad (L/m)$$

The preferred method of providing the purge gas is by using a membrane system which separates oxygen and nitrogen from air. Portable membrane units incorporating one or more hollow fibre cartridges are used to provide flexibility in gas flow and oxygen concentrations. The number, size and configuration of membrane cartridges will be determined by the purge gas flows and oxygen concentrations calculated from the container leakage parameters and produce respiration rates. Typical cartridges suitable for carrying out the invention are supplied by A.G. Technology Corporation of Boston, United States of America and are produced in a variety of sizes.

Further details on the construction and operation of membrane gas generation systems can be found in "Membrane Systems for Gas Generation in Remote Areas". "Rigby G.R. Engineering Conference Darwin, May 11-15, 1987". This paper is herein incorporated into the specification by reference.

Referring to Figure 3, compressed air 10 supplied from an oil lubricated compressor 11 is first passed through an air cooled after cooler, refrigerated drier, coalescing

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filter and activated carbon filter collectively shown as 12 to remove oil and water droplets. The dry filtered air 13 is then passed through a pressure regulation stage 14 before entering the membrane cartridges 15. The retentate (nitrogen enriched gas) flow 16 is throttled through a series of valves 17 before passing through a rotameter to the container. The oxygen rich permeate 18 is then discarded.

The separation of oxygen and nitrogen in the membrane occurs by a combination of solubilisation and diffusion through the ultra-thin non-porous polymeric separating layer according to equation (1).

$$Q_i = \frac{q_i}{A} = \frac{P_i \Delta p}{l} \quad (1)$$

and  $P_i = D_i S_i$

where

$\Delta p$  = pressure drop across the membrane, atm

$P_i$  = permeability of gas i,  $\text{m}^3 \text{mm}^{-2} \text{h}^{-1} \text{atm}^{-1}$

$D_i$  = diffusivity of gas i,  $\text{m}^2 \text{h}^{-1}$

$S_i$  = solubility of gas i in the membrane  
(Henry's Law sorption co-efficient),  
 $\text{m}^3 \text{m}^{-3} \text{atm}^{-1}$

$q_i$  = permeation flux of gas i  $\text{m}^3 \text{h}^{-1} \text{m}^{-2}$

$A$  = membrane area,  $\text{m}^2$

$l$  = thickness of membrane, m

$Q_i$  = flow of permeate gas  $\text{m}^3 \text{h}^{-1}$

For a given membrane,  $P_i$  and  $l$  are fixed and hence the retentate flowrate for a given oxygen concentration in the retentate is varied by adjusting the valve on the retentate outlet from the membrane and hence the relative proportion of feed air passing to the retentate stream. Figure 7 illustrates the typical variation in flow and oxygen concentration for the membrane cartridges at different pressures.

Since the oxygen concentration varies with retentate gas flowrate and flowrate varies with operating pressure, it is possible to vary both gas flowrate and oxygen concentration independently by adjusting the flowrate

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through the membrane and the operating pressure. This is achieved by two sets of solenoid valves, one to control pressure and the other to control flowrates. Figure 2 shows a schematic diagram of the overall container system and Figure 3 shows the arrangement of solenoid and needle valves.

In the refrigerated container 20 shown in Figure 2, the preferred membrane maintenance control unit comprises a gas sampling unit 21 and gas analysers 22 which provide information for the electronic control and data logging unit 23. The control and data logging unit 23 also receives information from thermocouples 24 located within the refrigerated container 20 and determines a suitable permeate flowrate and oxygen concentration for the membrane gas generation unit 25 and then adjusts the gas generation unit accordingly.

The appropriate flowrates and oxygen concentration for each set of valve settings in Figure 3 can be pre-adjusted for the product being transported. These settings will also vary for different container oxygen and carbon dioxide specifications. In situations where higher flowrates are required additional membrane surface area can be provided to deliver the required flows. The number of valves required to provide the desired level of control will depend on the produce and other container parameters. For example, with four valve settings, sixteen combinations of flow and oxygen concentration can be chosen by the computer programme in the control unit.

Alternative air supply systems and membrane arrangements may be used to optimise the equipment for specific container and produce requirements. An oil free compressor may be used as an alternative to the oil lubricated unit, thereby eliminating the need for oil removal. Some membranes permit operation at higher temperatures and reduce the need for extensive air cooling.

The atmosphere in the container is first reduced to approximately the desired oxygen and carbon dioxide level

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and then the control maintenance system of the invention is used.

The initial atmosphere in the container may be established using a separate system to that used for the maintenance during transportation. The gas flows for this operation are very much higher than those required for the maintenance phase, since it is preferable to establish these conditions quickly after loading. For example, with stone fruit it is essential to establish the desired  $O_2$  and  $CO_2$  levels within 12 hours of loading to gain the maximum effect of controlled atmosphere storage.

The initial conditions can be established using either a membrane gas generation system or by using a source of nitrogen from a cylinder or liquid storage facility. Nitrogen supplies from these latter sources are often unreliable, especially in remote areas. Membrane systems are self-contained and are often advantageous for this application. Therefore, it is preferable to minimise the size of the gas generation and control system, so that the complete unit is easily fitted and removed from the container when not required for controlled atmosphere generation. This has the added advantage that it can be easily relocated for subsequent use, whereas in-built systems are generally costly and containers are often difficult to relocate to the port required.

In some cases, where the fruit or vegetable respiration is low and high  $CO_2$  conditions are required for transportation (for example with stone fruit), the initial  $CO_2$  level is achieved by addition of supplementary  $CO_2$  from a gas cylinder.

A typical gas analyser used to measure the oxygen concentration in the container is a limiting current zirconia oxygen sensor developed and supplied by Fujikura Ltd. (type FCX). Carbon dioxide concentration is measured using an open path infra-red sensor by ADC Co. Ltd. (type WA456). These sensors were chosen and demonstrated to provide compact and cost effective gas analysis.

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Referring to Figure 1 the control system in accordance with the invention is illustrated for the above membrane system.

For a particular produce the optimum oxygen and carbon dioxide concentrations for storage are generally known or are determined by experimentation. Once known the  $O_2$  and  $CO_2$  concentration set points are set to correspond to these optimum values. The void volume is the space in the container which is not occupied by the produce and packaging. The produce respiration rate is determined by experimentation for a particular produce and varies with oxygen concentration, carbon dioxide concentration, maturity and temperature.

Container leakage rate is determined by experimentation utilising various purge gas flowrates and monitoring container oxygen concentration in the empty container or estimated from a pressure decay measurement on the empty container and is a function of the total gas flow purged into the container as shown in Figure 6. A mass balance is carried out by the electronic control unit using all these variables so that a first flowrate is determined to achieve the set points.

After a pre-determined time typically 15 - 30 minutes, the oxygen and carbon dioxide levels are tested. Using the measured  $O_2$  and  $CO_2$  as a basis, further mass balances are performed so that the oxygen and carbon dioxide levels at the next sample time are then predicted for each of the available membrane flows and  $O_2$  concentration combinations. The difference between the predicted levels and the set points is calculated and the flow/pressure valves are reset if necessary to the combination which gives the minimum difference.

In this way, if there is any discrepancy between the initial leakage and respiration rates and the actual values, the control maintenance system detects this as an oxygen or carbon dioxide concentration fluctuation and corrects accordingly.

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As can be seen, corrective action can be initiated if either the oxygen or carbon dioxide levels vary resulting in effective control of both gases.

Figure 5 shows a typical set of data for a trial involving 12 tonnes of Packham pears. The oxygen level was maintained by the controller and membrane system between a nominal level of 0.8% and 1.5% and the carbon dioxide level between 0.4% and 0.8% over a period of 40 days.

The increase in oxygen level to approximately 4% after 650 hours resulted from a power interruption. The data shows how the control unit re-established the desired conditions once the power was restored after a period of 24 hours.

Typical membrane gas purge flowrates were 20 litres/minute to 27 litres/minute with oxygen concentration in the flow between about 1.2% and 1.6%. These flows and concentrations will vary for different produce and time of storage. At the beginning of the trial, the respiration rate of CO<sub>2</sub> of the pears was calculated from the data to be 0.8 ml/kg,h. This level dropped to 0.55 ml CO<sub>2</sub>/kg,h at the end of the 40 day trial.

The system was trialed and demonstrated successfully on a shipment of asparagus over a 10,000 km voyage from Melbourne, Victoria, Australia to Japan. The shipment contained approximately 6.5 tonnes of asparagus. The set point to the controlled atmosphere O<sub>2</sub> and CO<sub>2</sub> concentrations was 5% and 8% respectively. The respiration rate for the asparagus calculated from the data was 8 ml/kg,h. The quality of the asparagus at the end of the trial was judged to be good to excellent.

A second shipment of blueberries transported from Melbourne to Belgium over a period of 35 days similarly demonstrated the suitability of the system to control CA conditions and maintain quality. The shipment contained approximately 4.3 tonnes of blueberries and nominal CA conditions of 1.5% O<sub>2</sub> and 6% CO<sub>2</sub> were readily maintained. The respiration rate for the blueberries was calculated

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from the data to be 2.2 ml/kg,h.

The significant differences in purge gas flows and O<sub>2</sub> concentrations for pears and blueberries (low respiration) and the asparagus (high respiration) illustrates the variations necessary for different produce and demonstrates the ability of the control and supply system to cope with these wide variations.

One other feature of the invention is the ability of the system to change the O<sub>2</sub> and CO<sub>2</sub> set points during the progress of the voyage and establish a further predetermined atmosphere. As an example, it may be desirable to maintain O<sub>2</sub> levels lower than 1% for a period to satisfy quarantine requirements. This level can then be adjusted (by appropriate software in the electronic control unit program) to the optimum level for long term storage. For some fruit and vegetables, a dynamic, or changing, controlled atmosphere regime may be desirable. This invention allows these conditions to be readily achieved.

To maximise the effectiveness of controlled atmosphere storage it is important to bring the atmosphere in the cool room or container down to the desired level as quickly as possible. It has been found that to minimise the pull down time a variable purge gas flowrate and oxygen concentration is more effective than a constant purge gas flowrate and oxygen concentration. For membrane systems with a constant pressure drop across the membrane the higher the flowrate used the higher the oxygen content of the gas. It has been thought that the quickest way to "pull down" a container was to use a purge gas with a low oxygen content. It has been found that much quicker "pull down" can be achieved by using a variable purge gas flowrate. Optimisation has found that by using a flowrate where the oxygen content of the purge gas is about one half of the instantaneous oxygen concentration in the cool store a container pull down rate greatly superior to constant flow and oxygen concentration can be achieved. Figure 1 and table 1 illustrate the effect for a commercial cool store. The times are longer



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than those generally required for containers but the principle is the same.

In practice "pull down" can be controlled automatically or manually in a stepwise manner.

As noted previously, "pull down" can also be achieved utilising an external supply of nitrogen from cylinders or liquid storage.

TABLE 1

COMPARATIVE "PULL DOWN" TIMES FOR CA COOL STORE TRIALS

Membrane Gas Flow Nm <sup>3</sup> /h	Membrane Gas O <sub>2</sub> Conc. %	Time to Reach 5%O <sub>2</sub> 3%O <sub>2</sub> in store, hours	
22.0	Variable	6.8	65      100
9.3		2.6	
6.8		1.8	
6.8		1.8	98      135
10.0		3.0	82      130

Although the present invention accounts for variations in container air leakage, it is still necessary to maintain these levels below a level at which the maintenance control system is effective and to minimise the capacity and cost of the membrane system.

For some produce, container leakage levels of less than 50 litres/h are essential. If the respiration rate of the produce is high, a higher leakage rate can be tolerated.

For very low respiring products, where high CO<sub>2</sub> levels are required during transportation (up to 6-8% CO<sub>2</sub>) a small supplementary purge gas flow of CO<sub>2</sub> from a cylinder may be required.

The maintenance of suitable relative humidity levels around the produce in the container is desirable to ensure that produce weight losses are not excessive. Some container systems utilise a separate humidity control system involving the addition of water to the gas stream or

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container. However, these systems are relatively costly, sometimes unreliable and can result in condensation of water droplets on the produce (resulting in a deterioration in quality).

Applicant has found that a more convenient means of maintaining the required humidity levels in a standard container around the produce is to use suitable wrappings. For example, with blueberries, the individual punnets have been wrapped with a permeable plastic film (with or without holes) and for pears and asparagus, an internal or external carton liner bag has been devised. Produce weight losses and quality have been shown to be quite satisfactory using these techniques.

Since the purge gas produced from the membrane has a relatively low humidity, it can be humidified simply by bubbling through a bath of water. Although initial trials utilised this system, subsequent trials have shown that this step is not essential for the low purge gas flows generally required. However, it remains an option for special gases or critical produce.

In order to maintain the leakage rates of the container for critical products, special care in container selection and sealing is essential. In addition, since leakage around the doors is impossible to eliminate completely, a plastic sheet or other convenient sealing device 29 is installed at the back of the container before the doors are closed. It is also preferable to use compression type rubber seals on the doors in an attempt to minimise leakage. Sealing of inspection ports and openings around electrical cables and other fittings from the refrigeration unit is also essential.

Another feature which is useful to minimise air leakage is to use a "breather bag" 28 inside the container (above the produce). This acts as a pressure equaliser and minimises the effects of localised external temperature or pressure changes. A purge valve 27 may be located at the rear of the container to relieve pressure (and eliminate

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the possibility of breaking the seal) during the initial period after sealing the container when temperature inside the container is reduced to the desired level. Without a purge valve significant stretching of the plastic sheet may occur due to the low internal pressure created as the volume of air in the container decreases. This step is less critical if the produce and container are pre-chilled prior to loading and the loading time is kept to a minimum.

A pressure relief valve 30 using an oil seal is also fitted to the container to permit discharge of purge gas flow, and avoid excessive pressure in the container.

Control of ethylene is especially critical with some fruits and vegetables. To maintain ethylene levels within desired limits, a small compact ethylene removal unit 26 inside the container may be used. This unit consists of an ultra violet lamp system and catalyst to remove the ozone produced. However, it has been found that by continuously supplying purge gas in accordance with the invention ethylene levels in the case of some produce, remain within the desired limited without the use of the ethylene removal unit.

The claims form part of the disclosure of this specification.

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**CLAIMS:**

1. A method for monitoring and controlling the atmosphere of a container or cool storeroom, said atmosphere being substantially established at predetermined oxygen and carbon dioxide concentration set points, comprising the steps of

(a) using predetermined data on (i) the void volume and air leakage rate of the container and (ii) the oxygen usage and carbon dioxide production of the produce in the container, to determine a purge gas flowrate and oxygen which will achieve the predetermined oxygen and carbon dioxide concentrations and supplying purge gas accordingly,

(b) after a predetermined time, monitoring actual oxygen and carbon dioxide concentration levels in the container or storeroom and determining new values of the purge gas flowrate and oxygen concentration which will achieve the oxygen and carbon dioxide concentration set points and supplying purge gas at the determined flowrate and oxygen concentration, and

(c) repeating step (b) for duration of the time at which the atmosphere is to be maintained at said predetermined concentration set points.

2. The method for monitoring and controlling the atmosphere in accordance with claim 1 wherein the purge gas is provided by compressing air on one side of a membrane permeable to oxygen to produce an oxygen deficient retentate to be used as purge gas and an oxygen rich permeate.

3. The method for monitoring and controlling the atmosphere in accordance with claim 2 wherein the oxygen concentration of the purge gas is varied by changing the pressure drop across the membrane and the purge gas flowrate is varied by changing the inlet air pressure to the membrane.

4. A method for controlling the atmosphere of a

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container or cool storeroom comprising the steps of

(a) establishing an atmosphere having a predetermined oxygen and carbon dioxide concentration by purging the container or storeroom with a purge gas,

(b) using predetermined data on (i) the void volume and air leakage rate in the container or cool storeroom and (ii) carbon dioxide production and oxygen usage of the produce in the container or cool storeroom to determine a purge gas flowrate and oxygen concentration which will achieve the predetermined oxygen and carbon dioxide concentrations and supplying said purge gas accordingly,

(c) after a predetermined time, monitoring actual oxygen and carbon dioxide levels in the container or storeroom and determining new values of purge gas flowrate and oxygen concentration which will achieve the oxygen and carbon dioxide concentration set points,

(d) supplying said purge gas at the purge gas flowrate and oxygen concentration determined in (c), and

(e) repeating step (c) and (d) for the duration of the time at which the atmosphere is to be maintained at the predetermined concentration set points.

5. The method for controlling an atmosphere of a container or cool storeroom in accordance with claim 4 the purge gas to establish the atmosphere and the purge gas to maintain the atmosphere are provided by separate purge gas units.

6. The method for controlling an atmosphere of a container or cool storeroom in accordance with one of the claims 4 or 5 wherein at least the purge gas for maintaining the atmosphere is provided by compressing air on one side of a membrane permeable to oxygen to produce an oxygen deficient retentate which is used as purge gas and an oxygen rich permeate.

7. The method for controlling an atmosphere of a

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container or cool storeroom in accordance with claim 6 wherein the oxygen concentration of the purge gas is varied by changing the pressure drop across the membrane and the purge gas flowrate is varied by changing the inlet air pressure to the membrane.

8. The method for controlling an atmosphere of a container or cool storeroom in accordance with any one of claims 4 to 7 wherein the step of establishing an atmosphere of a predetermined oxygen and carbon dioxide concentration further comprises the step of monitoring the oxygen concentration in the container and varying the oxygen concentration in the purge gas flow such that the flowrate oxygen concentration is about one half the instantaneous oxygen concentration in the container.

9. The method for controlling an atmosphere in accordance with any one of claims 1 - 8 wherein an ethylene scrubber is activated when the ethylene produced by the produce in the container is determined to be above a predetermined level.

10. The method for controlling an atmosphere in accordance with any one of claims 1 - 9 wherein the predetermined oxygen and carbon dioxide set points are reset to change the conditions within the container or cool storeroom to a further predetermined atmosphere.

11. An apparatus for monitoring and controlling the atmosphere of a container or cool store once predetermined oxygen and carbon dioxide concentration set points have substantially been established comprising

(a) means to determine from (i) the void volume and air leakage rate of the container and (ii) oxygen usage and carbon dioxide production of the produce in the container, a purge gas flowrate and oxygen concentration which will achieve the predetermined oxygen and carbon dioxide

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concentration set points,

(b) means to supply purge gas at the flowrate and oxygen concentration determined in (a),

(c) means to monitor the oxygen and carbon dioxide concentration in the container after a predetermined time and determining new values for the purge gas flowrate and oxygen concentration to achieve the predetermined set points, and

(d) means to adjust the purge gas flowrate and oxygen concentration to the values determined in (c).

12. An apparatus for monitoring and controlling the atmosphere of a container or cool store in accordance with claim 11 wherein the means to supply purge gas comprises a membrane separation unit whereby air is compressed on one side of a membrane permeable to oxygen resulting in an oxygen deficient retentate which is used as a purge gas and an oxygen rich permeate.

13. The apparatus for monitoring and controlling the atmosphere of a container or cool storeroom in accordance with claim 12, wherein the oxygen concentration of the purge gas is varied by changing the pressure drop across the membrane and the purge gas flowrate is varied by changing the inlet air pressure to the membrane.

14. An apparatus for controlling the atmosphere in a container or cool storeroom comprising

(a) a means to establish the atmosphere at predetermined oxygen and carbon dioxide set points,

(b) means to determine from predetermined data on (i) the void volume and rate of air leakage for the container or cool store and (ii) oxygen usage and carbon dioxide production of the produce in the container or cool store a purge gas flowrate and oxygen concentration which will maintain the oxygen and carbon dioxide set points,

(c) means to supply purge gas at the determined

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flowrate and oxygen concentration to maintain the atmosphere,

(d) means to monitor the oxygen and carbon dioxide concentration in the container after a predetermined time and determine new values of purge gas flowrate and oxygen concentration which will maintain the predetermined set points, and

(e) means to adjust the purge gas supply to the new values of purge gas flowrate and oxygen concentration.

15. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with claim 14, wherein the means to supply purge gas comprises a membrane separation unit whereby air is compressed on one side of a membrane permeable to oxygen resulting in an oxygen deficient retentate which is used as a purge gas and an oxygen rich permeate.

16. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with claim 15, wherein the oxygen concentration of the purge gas is varied by changing the pressure drop across the membrane and the purge gas flowrate is varied by changing the inlet air pressure to the membrane.

17. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with any one of claims 14 - 16 wherein the means to establish the atmosphere is capable of supplying a purge gas such that the oxygen concentration of the purge gas is about one half the instantaneous oxygen concentration of the atmosphere in the container or cool store.

18. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with any one of claims 14, 15, 16 or 17 wherein the means to establish the atmosphere comprises a membrane separation unit.



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19. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with claim 18, whereby the means to establish the atmosphere and the means to maintain the atmosphere are separate units.

20. The apparatus for controlling the atmosphere of a container or cool storeroom in accordance with any one of claims 12 - 19 wherein an ethylene scrubber is provided to maintain the concentration of ethylene in the container or cool store below a predetermined level.

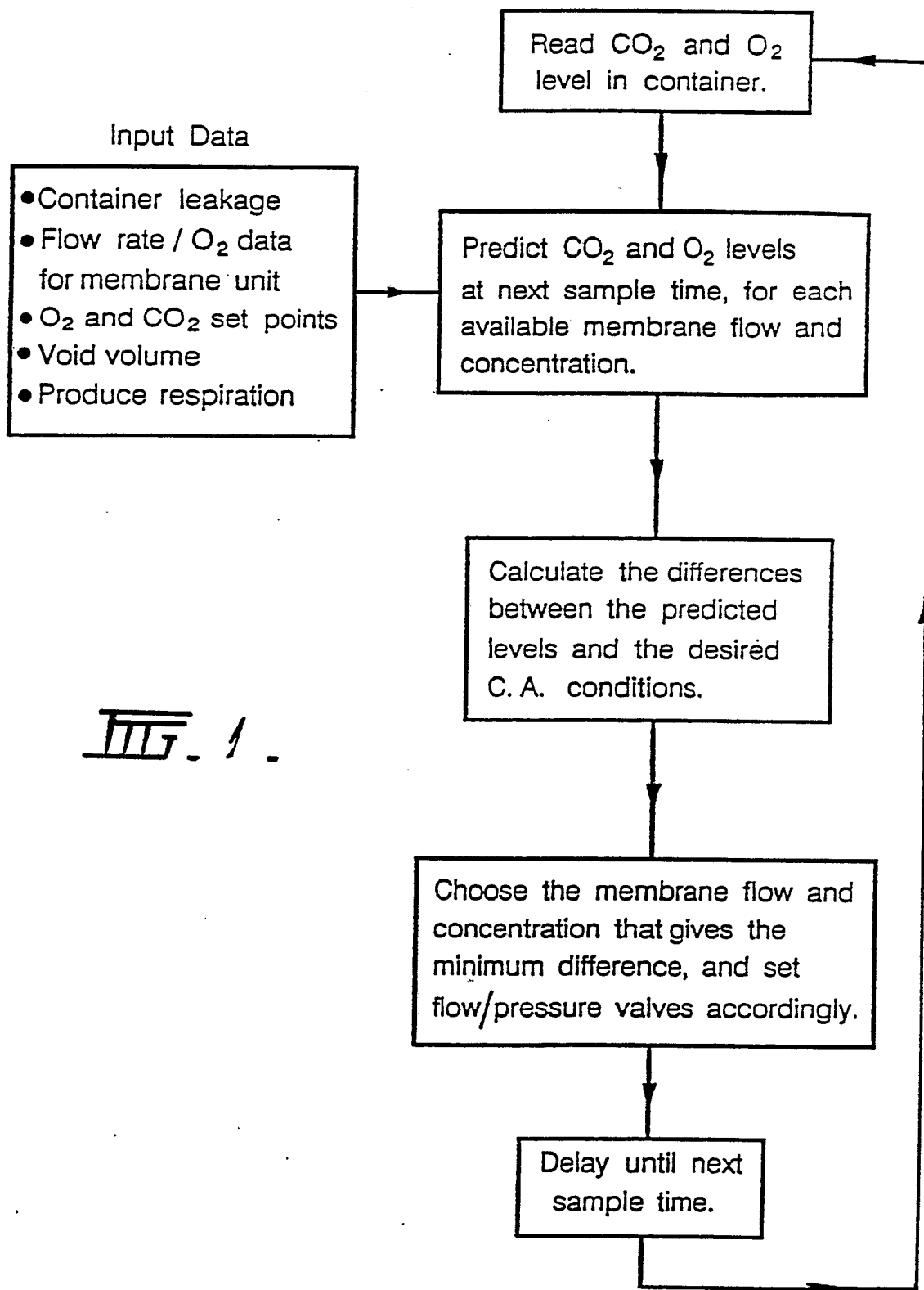
21. The apparatus in accordance with any one of claims 10 - 19 wherein there is provided a means to reset the carbon dioxide and oxygen concentration set points to achieve a further predetermined atmosphere.

22. A container or storeroom whose atmosphere is maintained by the method in accordance with any one of claims 1 to 3.

23. Produce conditioned by the method in accordance with any of claims 1 to 10.

24. Produce conditioned by the apparatus in accordance with any one of claims 11 to 20.

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FIG. 1.

SUBSTITUTE SHEET

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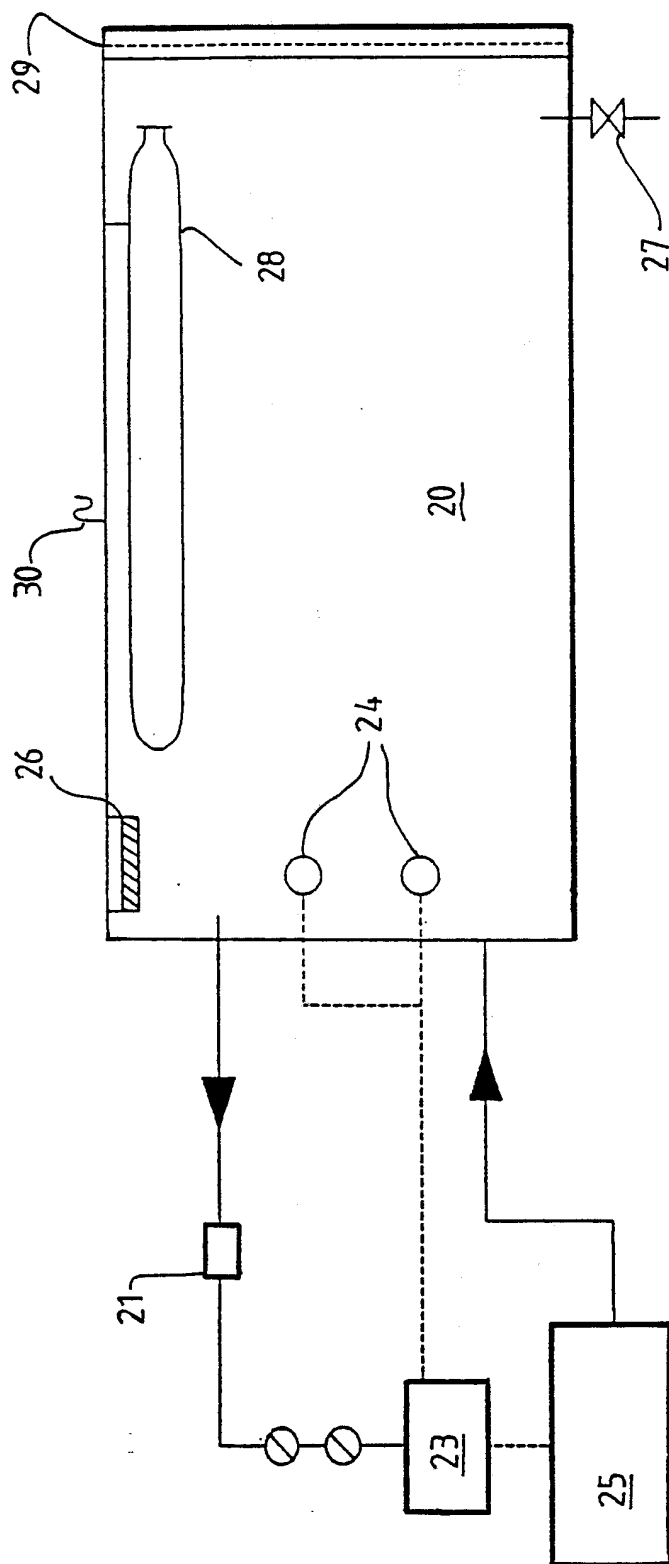
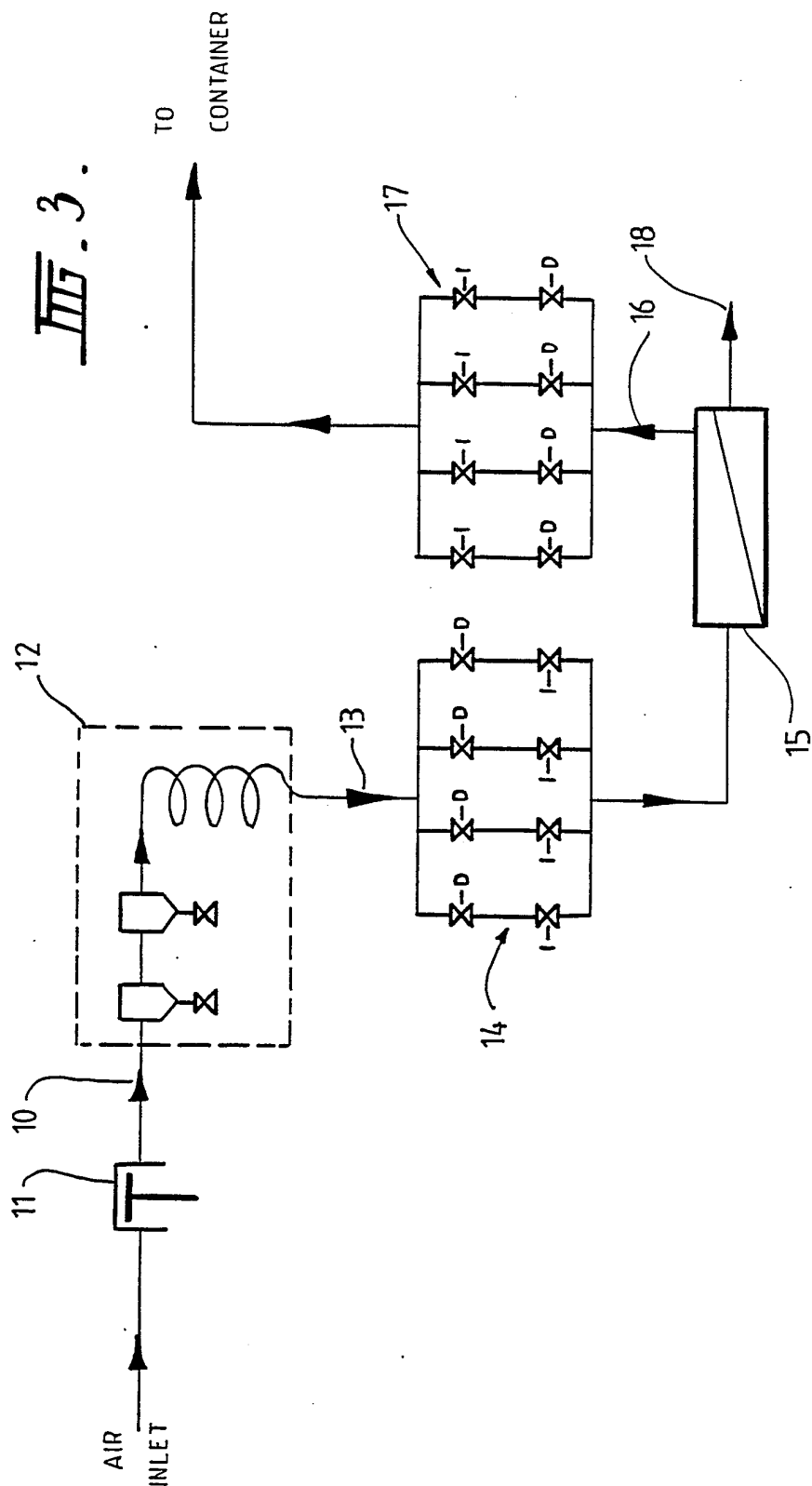


Fig. 2.

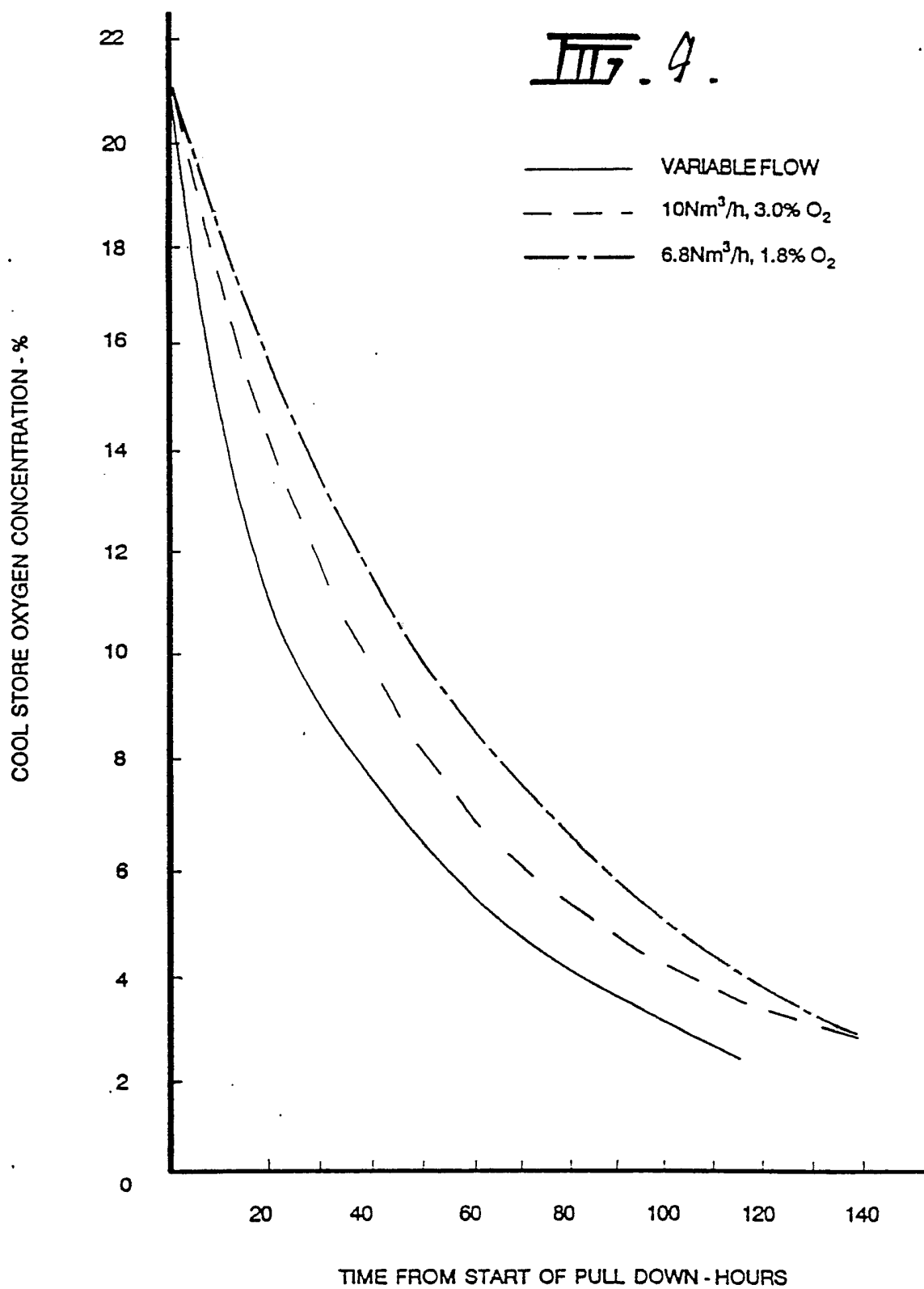
SUBSTITUTE SHEET

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SUBSTITUTE SHEET

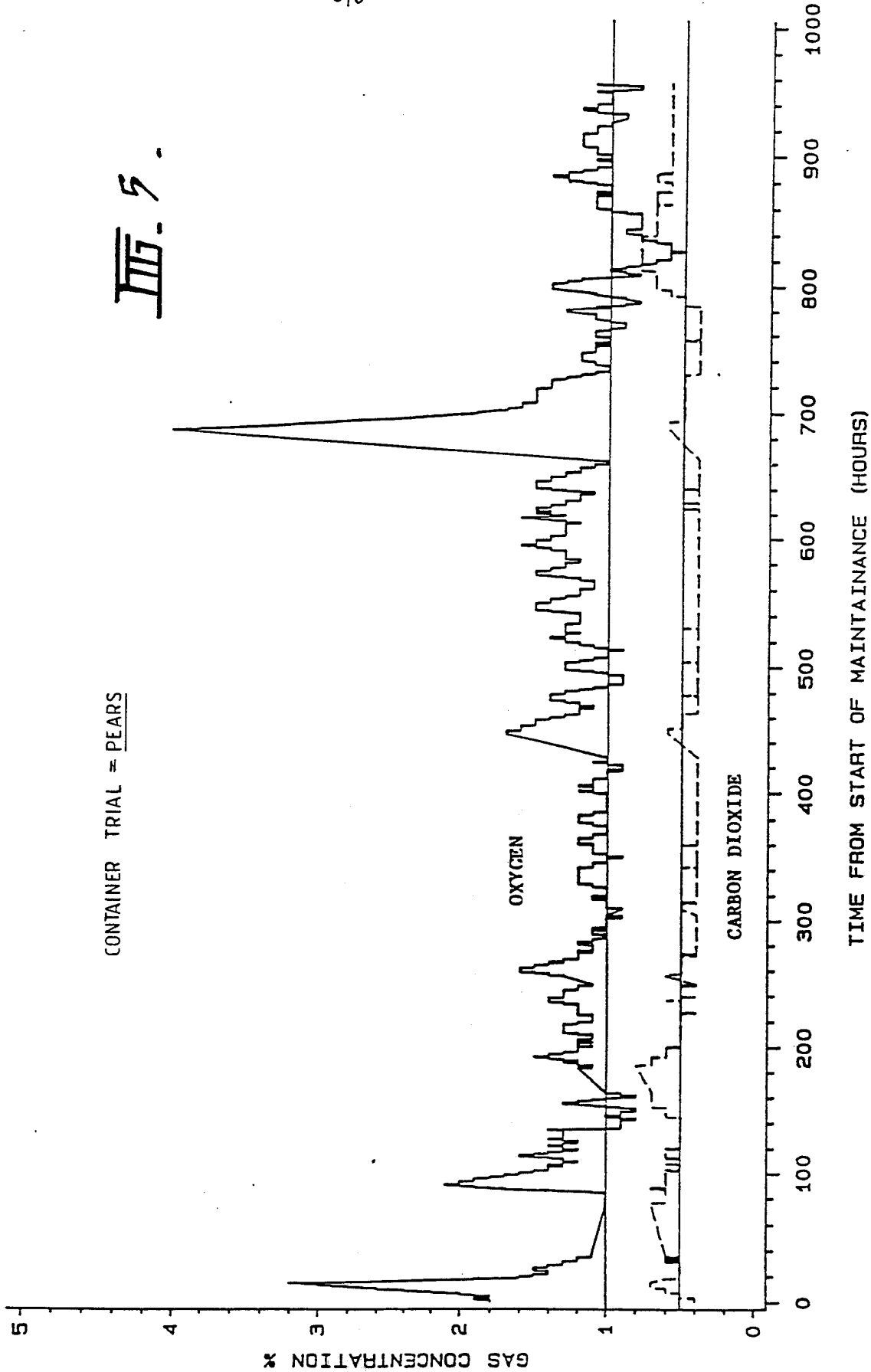
4/8

**SUBSTITUTE SHEET**

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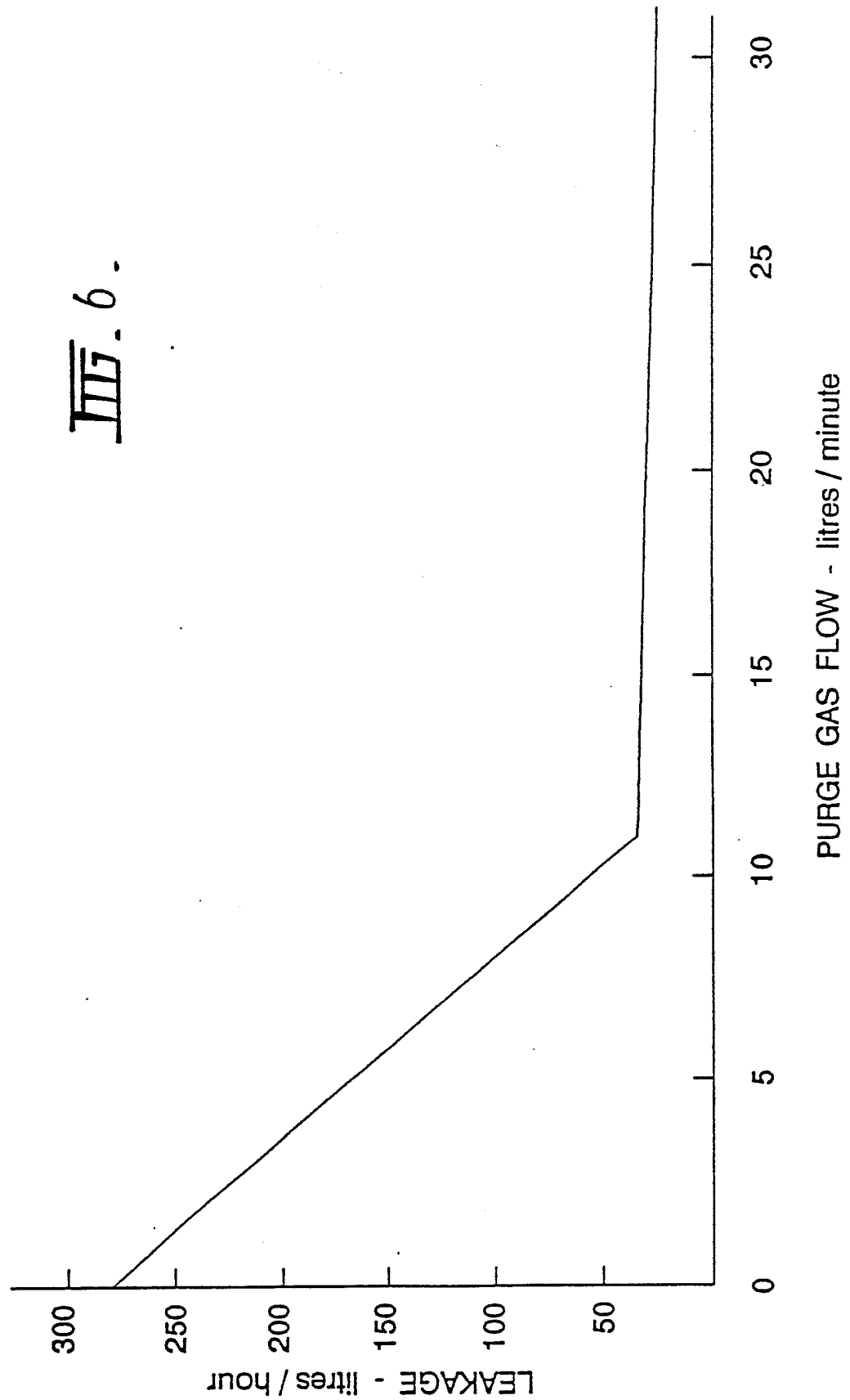
Fig. 5.

CONTAINER TRIAL = PEARS



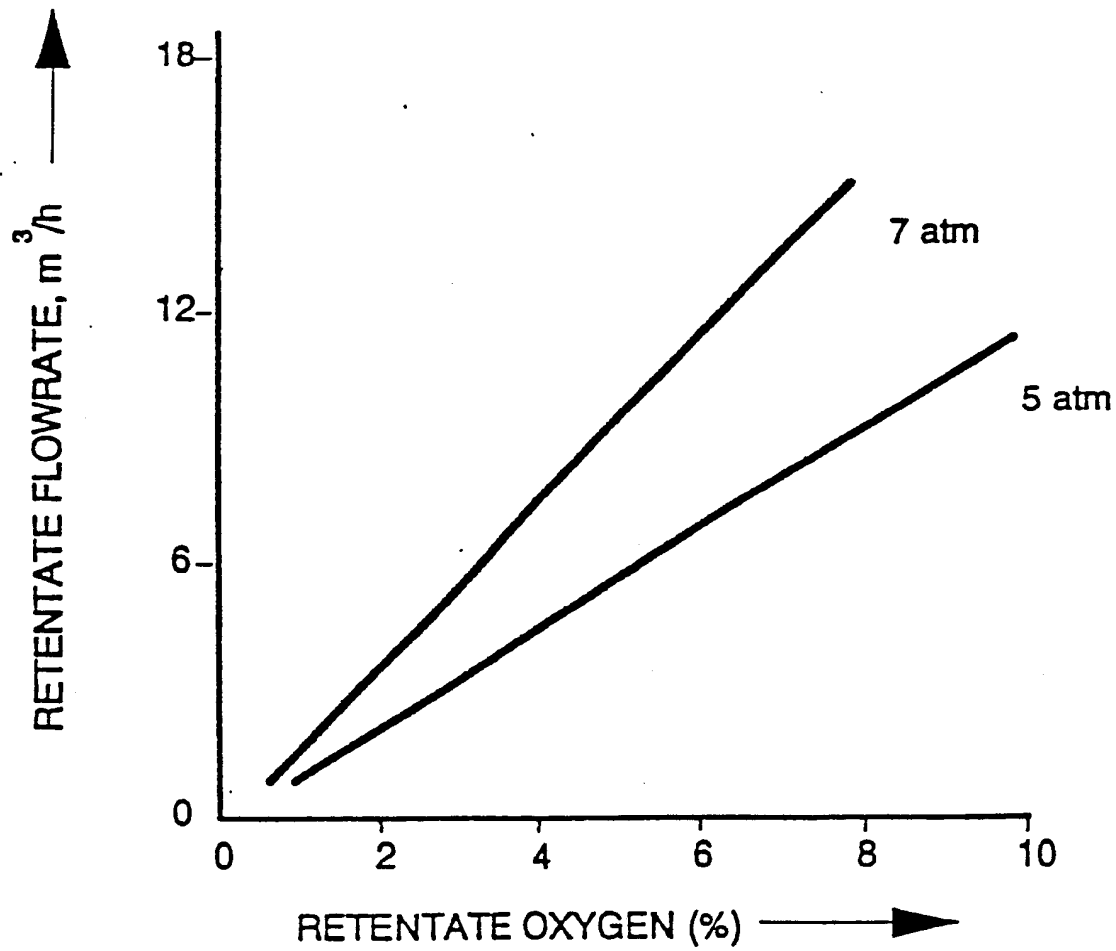
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III. 6.



SUBSTITUTE SHEET

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FIG. 7.



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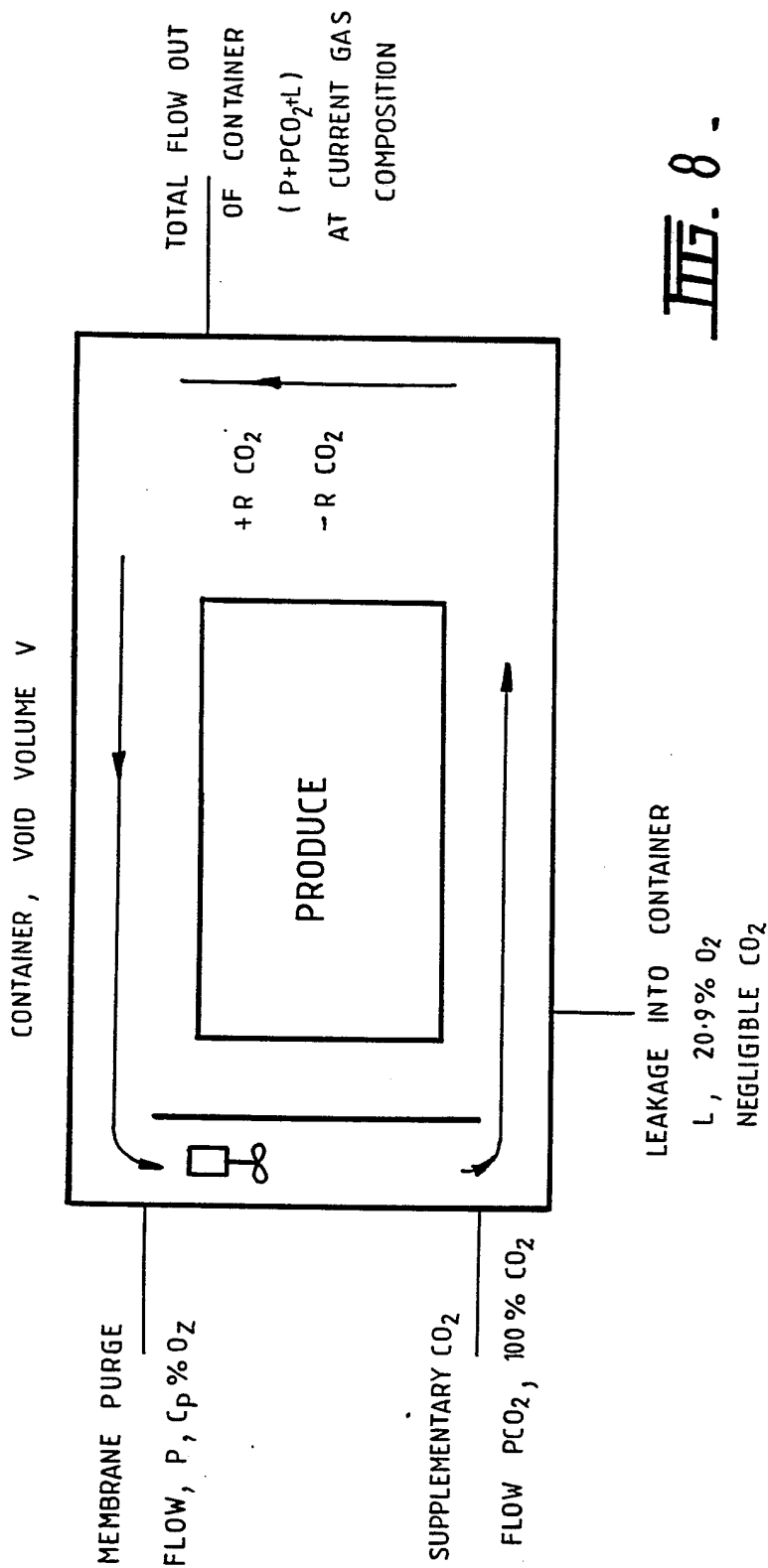


Fig. 8.

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/AU 91/00049**

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.<sup>5</sup> A23B 7/148, 7/152

## II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
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IPC	A23B 7/148, 7/152; A23L 3/3418, 3/3445
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Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched 8

AU: IPC as above

## III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, <sup>11</sup> with indication <sup>12</sup> where appropriate, of the relevant passages	Relevant to Claim No 13
P,X	Patent Abstracts of Japan, C-771, page 153, JP,A, 2-200144 (TELJIN LTD), 8 August 1990 (08.08.90)	1-24
P,X	AU,A, 44577 (TRANSPHERE SYSTEMS LIMITED) 17 May 1990 (17.05.90)	1-24
P,X	EP,A, 363553 (ISOLCELL ITALIA SpA) 18 April 1990 (18.04.90)	1-10
X	EP,A, 353021 (TRANSFRESH CORPORATION) 31 January 1990 (31.01.90)	1-24
A	US,A, 4894997 (URUSHIZAKI et al) 23 January 1990 (23.01.90)	1-10
X	Patent Abstracts of Japan, C-688, page 153, JP,A, 1-296940 (NATAL FOOD RES INST), 30 November 1989 (30.11.89)	1-24
X	AU,A, 22875/88 (NICAP INC) 4 May 1989 (04.05.89)	1-24
A	AU,A, 79395/87 (HERCULES INC) 14 April 1988 (14.04.88)	1-10
X	AU,B, 32431/84 (567966) (SHIPPING CORP OF NEW ZEALAND LTD; THE NEW ZEALAND GOVERNMENT PROPERTY CORP) 7 March 1985 (07.03.85)	1-24

\* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search  
8 May 1991 (08.05.91)

Date of Mailing of this International Search Report

**13 MAY 1991**

International Searching Authority

Signature of Authorized Officer

**Australian Patent Office**

**J BODEGRAVEN**

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
  
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
  
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.  
☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON  
INTERNATIONAL APPLICATION NO. PCT/AU 91/00049

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Members				
AU	44577	CA	2002754	EP	368678	JP	2242612
AU	22875	EP	315309	US	4817391	ZA	8807097
AU	79395	BR	8705295	CN	87107591	DK	5237/87
		EP	270764	IL	84100	JP	63152638
		NZ	222065	US	4842875		
AU	32431	EP	136042	JP	61025443	NZ	205453
		US	4642996	US	4716739	ZA	8406661
US	4894997	EP	292834	JP	63283538	JP	63283539
EP	363553	JP	2098581				
EP	353021	AU	38968/89	JP	2167027	US	4987745

END OF ANNEX

**PUB-NO:** WO009111913A1  
**DOCUMENT-IDENTIFIER:** WO 9111913 A1  
**TITLE:** CONTROLLED ATMOSPHERE  
GENERATION IN HORTICULTURAL  
APPLICATIONS  
**PUBN-DATE:** August 22, 1991

**INVENTOR-INFORMATION:**

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DARATECH PTY LTD	AU

**APPL-NO:** AU09100049  
**APPL-DATE:** February 13, 1991

**PRIORITY-DATA:** AU00PJ861990A (February 13, 1990)

**INT-CL (IPC):** A23B007/148 , A23B007/152

**EUR-CL (EPC):** A23B007/152 , A23B007/148 ,  
A23L003/3481

**US-CL-CURRENT:** 426/324 , 426/419

**ABSTRACT:**

CHG DATE=19990617 STATUS=O>A method and apparatus is described for monitoring and controlling the concentrations of oxygen and carbon dioxide in the atmosphere of a storage container or cool storeroom. The invention uses a knowledge of (a) the oxygen usage and carbon dioxide production rates of the produce stored and (b) the void volume and air leakage rate of the container or cool storeroom to determine a purge gas flowrate and oxygen concentration which will maintain the preset concentrations of oxygen and carbon dioxide. A permeable membrane gas separation unit is preferably used to provide the purge gas which is generated by compressing air on one side of the membrane permeable to oxygen to produce an oxygen deficient retentate and an oxygen rich permeate.